

DESCRIPTION

SEPARATOR FOR ALKALINE BATTERIES AND BATTERY USING SAME

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TECHNICAL FIELD

The present invention relates to a separator for alkaline batteries and an alkaline battery using the separator. More particularly, the present invention relates to a separator for alkaline batteries which exhibits an improved discharging property (in particular, an improved discharging property at high temperatures) and an improved discharging property under a great load and an alkaline battery equipped with the separator.

15 BACKGROUND ART

Recently, portable information instruments requiring the excellent discharging property under a great load such as digital cameras are widely used. When a conventional battery is used for the portable information instruments requiring the discharging property under a great load, the capacity of the battery decreases in a short time since conventional batteries have short lives. The battery must be replaced with a fresh battery every time the capacity of the battery decreases, and it is difficult that the instruments are utilized smoothly. Moreover, since the application and the mode of utilization of batteries diversify, batteries are frequently exposed to high temperatures during storage, during periods without discharge and during periods with discharge (during the

use of the instruments). Conventional batteries exhibit rapid deterioration in the discharging property when the batteries are exposed to high temperatures.

As the means for improving the discharging property of alkaline batteries under a great load, it is proposed that an active substance for the positive electrode prepared by adding nickel oxyhydroxide to manganese dioxide is used in an alkaline battery having a positive electrode mix, a negative electrode made of zinc and an alkaline electrolyte (an alkaline aqueous solution) and the proposed means has been used for practical applications (for example, Japanese Patent Application Laid-Open No. Showa 57(1982)-49468).

For improving the discharging property under a great load, the storage property and the resistance to leakage of the liquid, it is proposed that a material prepared by adding polyethylene powder to the combination of manganese dioxide and nickel oxyhydroxide is used as the positive electrode mix (for example, Japanese Patent Application Laid-Open Nos. 2001-32250 and 2001-332249).

In conventional alkali batteries, non-woven fabrics formed by using a synthetic fiber such as a polyvinyl alcohol-based fiber, a polyolefin-based fiber and a polyamide fiber or a mixed fiber obtained by adding a cellulose fiber to the synthetic fiber as the main fiber are used as the separator.

Among the above non-woven fabrics, non-woven fabrics formed by using an aliphatic polyamide fiber such as nylon 6 and nylon 66 have advantages in that the property for holding the electrolyte is excellent and the capacity of discharge is great due to the excellent resistant to alkalis and the hydrophilic property. However, the above non-woven fabrics

have a drawback in that, when the fabrics are used as the separator for alkaline batteries, the fabrics tend to be degraded by oxidation with oxygen gas generated during charging due to poor resistance to degradation by oxidation at high temperatures. In particular, the fabrics
5 tend to be degraded more easily by oxidation when the fabrics are used for secondary batteries which are repeatedly charged and discharged at high temperatures.

To improve the resistance of the polyamide fiber to degradation by oxidation, it is proposed that a separator for batteries is formed with a
10 mixture or a composite of a polyamide fiber and a polyolefin fiber (for example, Japanese Patent Application Laid-Open Nos. Showa 55(1980)-25921 and Showa 55(1980)-66864). The degradation by oxidation can be decreased to some degree due to the decrease in the content of the polyamide fiber. However, the improvement is not
15 sufficient and the problem is not overcome fundamentally.

It is proposed that a non-woven fabric formed with an aromatic polyamide fiber or an entirely aromatic polyamide fiber in place of the aliphatic polyamide is used for the separator for batteries (for example, Japanese Patent Application Laid-Open Nos. Showa 58(1983)-147956 and
20 Heisei 5(1993)-289054). However, the non-woven fabric constituting this separator for batteries has poor strength since the fiber constituting the separator has a high melting point and exhibits poor adhesion with a thermoplastic binder fiber although the separator exhibits excellent hydrophilic property, resistance to alkalis and resistance to degradation
25 by oxidation.

From the above standpoint, the present inventors have been

studying to develop a separator for batteries which exhibits excellent hydrophilic property, resistance to alkalis, property for holding alkaline electrolytes, resistance to degradation by oxidation and adhesion to binder fibers. It was found that a separator for batteries exhibiting the
5 excellent hydrophilic property, resistance to alkalis, property for holding alkaline electrolytes, resistance to degradation by oxidation and adhesion with binder fibers could be obtained when a separator for batteries was formed by using a fiber formed, as the main fiber component, with a polyamide which was synthesized from a dicarboxylic acid component
10 containing 60% by mole or more of an aromatic dicarboxylic acid and a diamine component containing 60% by mole or more of an aliphatic alkylenediamine having 6 to 12 carbon atoms such as 1,9-nonanediamine and 2-methyl-1,8-octanediamine. Patents have been applied based on the above finding (Japanese Patent Application Laid-Open Nos. Heisei
15 9(1997)-259856 and 2002-151041).

The present inventors conducted further studies based on the inventions disclosed in Japanese Patent Application Laid-Open Nos. Heisei 9(1997)-259856 and 2002-151041 described above, and it was recognized that, for an alkaline battery using, as the positive electrode
20 mix, manganese dioxide added with an agent having a great oxidizing ability for enhancing the discharging property under a great load such as nickel oxyhydroxide, it was urgently necessary that a separator for alkaline batteries which exhibited more excellent resistance to degradation by oxidation at high temperatures than that of the battery
25 described above, was not degraded by oxidation with nickel oxyhydroxide added to the positive electrode mix even when the separator was exposed

to high temperatures for a long time, for example, even when the separator was stored at high temperatures, could maintain a great capacity of the positive electrode (the capacity of the battery) for a long time and, therefore, could maintain the excellent discharging property under a great load, be developed.

The present invention has an object of providing a separator for alkaline batteries which, when the separator is used for an alkaline battery using, as the positive electrode mix, manganese dioxide added with an agent having a great oxidizing ability for enhancing the discharging property under a great load such as nickel oxyhydroxide, is not degraded by oxidation with nickel oxyhydroxide added to the positive electrode mix even when the separator is exposed to high temperatures for a long time, for example, even when the separator is stored at high temperatures, can maintain a great capacity of the positive electrode (the capacity of the battery) for a long time and, therefore, can maintain the excellent discharging property under a great load.

The present invention has a further object of providing an alkaline battery equipped with the separator for alkaline batteries described above.

DISCLOSURE OF THE INVENTION

As the result of intensive studies by the present inventors to achieve the above objects, it was found that, when a specific cellulose fiber, i.e., a solvent-spun cellulose fiber produced by using a spinning solution prepared by dissolving cellulose into a non-reactive solvent, was used in combination with a fiber comprising a polyamide constituted with a

dicarboxylic acid unit mainly containing the terephthalic acid unit and a diamine unit mainly containing the 1,9-nonanediamine unit or the 1,9-nonanediamine unit and the 2-methyl-1,8-octanediamine unit, such as the fibers described in Japanese Patent Application Laid-Open Nos. 5 Heisei 9(1997)-259856 and 2002-151041 described above, and a separator for alkaline batteries was formed by using the above fibers as the main component fibers, the obtained separator for batteries showed less degradation of the polyamide fiber in the separator with the positive electrode mix than that in conventional separators for batteries even 10 when the separator is exposed to high temperatures for a long time, for example, even when the separator is stored at high temperatures, and that, due to this effect, the decrease in the capacity of the battery was further suppressed when an alkaline battery was prepared by using the separator for alkaline batteries and the discharging property of the 15 alkaline battery under a great load was further improved.

It was also found by the present inventors that, when the polyamide fiber constituting the separator in the above separator for alkaline batteries was formed with a polyamide having sealed chain ends, the polyamide fiber exhibited further improved oxidation resistance, 20 hydrolysis resistance, water resistance and heat resistance, and the separator for alkaline batteries exhibited further improved oxidation resistance, hydrolysis resistance, water resistance and heat resistance.

It was also found by the present inventors that, when the main component fibers are adhered together using a fiber-shaped binder in the separator for alkaline batteries using the above specific polyamide fiber 25 and a cellulose fiber as the main component fibers, a separator exhibiting

excellent strength and property for separation could be obtained. The present invention has been completed based on the above knowledge.

The present invention provides:

(1) A separator for alkaline batteries (i) which comprises a non-woven fiber structural material comprising a polyamide fiber and a cellulose fiber as main component fibers, wherein

(ii) the polyamide fiber is a fiber formed with a polyamide constituted with a dicarboxylic acid unit and a diamine unit, the dicarboxylic acid unit comprising 60% by mole or more and 100% by mole or less of a terephthalic acid unit and the diamine unit comprising 40% by mole or more and 99% by mole or less of a 1,9-nonanediamine unit;

(iii) the cellulose fiber is a solvent-spun cellulose fiber produced by using a spinning solution prepared by dissolving cellulose into a non-reactive solvent; and

(iv) a ratio of an amount by mass of the polyamide fiber to an amount by mass of the cellulose fiber in the non-woven fiber structural material is in a range of 20:80 to 80:20.

The present invention further provides:

(2) A separator for alkaline batteries described in (1), wherein the polyamide forming the polyamide fiber comprises a 2-methyl-1,8-octanediamine unit in combination with the 1,9-nonanediamine unit, and a ratio of an amount by mole of the 1,9-nonanediamine unit to an amount by mole of the 2-methyl-1,8-octanediamine unit in the polyamide is in a range of 99:1 to 40:60.

The present invention further provides:

(3) A separator for alkaline batteries described in any one of (1) and (2),

wherein the polyamide forming the polyamide fiber has a fraction of sealed chain ends of 10% or greater.

The present invention further provides:

- (4) A separator for alkaline batteries described in any one of (1) to (3),
5 wherein a size of a single fiber in the polyamide fiber is in a range of 0.01 to 1.0 dtex.

The present invention further provides:

- (5) A separator for alkaline batteries described in any one of (1) to (4),
wherein the cellulose fiber is a solvent-spun cellulose fiber obtained by
10 dry-wet spinning in water of a spinning solution prepared by dissolving cellulose into an amine oxide.

The present invention further provides:

- (6) A separator for alkaline batteries described in any one of (1) to (5),
wherein the main component fibers are adhered together with a
15 fiber-shaped binder.

The present invention further provides:

- (7) A separator for alkaline batteries described in (6), wherein an
amount of the fiber-shaped binder is in a range of 3 to 30% by mass based
on a total of an amount by mass of the main component fibers and an
20 amount by mass the fiber-shaped binder.

The present invention further provides:

- (8) An alkaline battery which is equipped with a separator for alkaline
batteries described in any one of (1) to (7).

25 THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

The present invention will be described in detail in the following.

The separator for alkaline batteries of the present invention comprises a non-woven fiber structural material comprising a polyamide fiber and a cellulose fiber as main component fibers.

5 The "non-woven fiber structural material" means a fiber structural material formed not by weaving or knitting the above main component fibers but by adhesion and/or entanglement of the above main component fibers with each other and includes non-woven fabrics having a flat sheet shape, materials having a shape of paper, materials having a shape of a cylinder, materials having a shape of a cylinder with a bottom and non-woven fiber structural materials having other shapes.

The polyamide fiber which is one of the main component fibers constituting the separator for alkaline batteries is formed with a dicarboxylic acid unit and a diamine unit.

15 It is necessary that the polyamide comprise 60% by mole or more, preferably 75% by mole or more and more preferably 90% by mole or more and 100% by mole or less of the terephthalic acid unit based on the entire amount of the dicarboxylic acid unit constituting the polyamide. When the amount of the terephthalic acid unit in the polyamide is less than 60% by mole, the properties such as the oxidation resistance, the chemical resistance and the heat resistance of the polyamide fiber become inferior and such an amount is not preferable.

25 The polyamide forming the polyamide fiber may comprise other dicarboxylic acid units in combination with the terephthalic acid unit as long as the amount of the other dicarboxylic acid units is 40% by mole or less. Examples of the other dicarboxylic acid unit include structural

units derived from aliphatic dicarboxylic acids such as malonic acid, dimethylmalonic acid, succinic acid, 3,3-diethylsuccinic acid, glutaric acid, 2,2-dimethylglutaric acid, adipic acid, 2-methyladipic acid, trimethyladipic acid, pimellic acid, azelaic acid, sebacic acid and suberic acid; structural
5 units derived from alicyclic dicarboxylic acids such as 1,3-cyclopentane-dicarboxylic acid and 1,4-cyclohexanedicarboxylic acid; and structural units derived from aromatic dicarboxylic acids such as isophthalic acid, 2,6-naphthalenedicarboxylic acid, 1,4-phenylenedioxane-diacetic acid, 1,3-phenylenedioxanediadicetic acid, diphenic acid, 4,4'-oxydibenzoic acid,
10 diphenylmethane-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid and 4,4'-biphenyldicarboxylic acid. The polyamide may comprise the dicarboxylic acid unit described above singly or in combination or two or more.

When the polyamide forming the polyamide fiber comprises the
15 other dicarboxylic acid units in combination with the terephthalic acid unit as the dicarboxylic acid unit, it is preferable that the polyamide comprises aromatic dicarboxylic acid units other than the terephthalic acid unit from the standpoint of the oxidation resistance, the chemical resistance and the heat resistance.

20 The polyamide may further comprise, where necessary, structural units derived from polybasic carboxylic acids having a functionality of three or greater such as trimellitic acid, trimesic acid and pyromellitic acid as long as the amount is small and the melt spinning can be conducted.

25 It is necessary that the polyamide fiber which is one of the main component fibers constituting the separator for alkaline batteries of the

present invention comprise 40% by mole or more of the 1,9-nonanediamine unit based on the entire amount of the diamine units constituting the polyamide so that the oxidation resistance, the heat resistance, the hydrolysis resistance and the dimensional stability of the polyamide fiber are improved and, as the result, these properties of the separator for alkaline batteries using the polyamide are improved. It is preferable that the polyamide fiber comprises 50% by mole or more and 99% by mole or less of the 1,9-nonanediamine unit.

In particular, it is preferable that the polyamide forming the polyamide fiber comprises the 2-methyl-1,8-octanediamine unit as the diamine unit in combination with the 1,9-nonanediamine unit since the oxidation resistance, the chemical resistance, the heat resistance and the hydrolysis resistance of the polyamide fiber are further improved.

When the polyamide forming the polyamide fiber comprises both of the 1,9-nonanediamine unit and the 2-methyl-1,8-octanediamine unit, it is preferable that the total of the amounts of the both units is in the range of 60 to 100% by mole and preferably in the range of 80 to 100% by mole based on the entire amount of the diamine units constituting the polyamide. In this case, it is preferable that the ratio of [the amounts by mole of the 1,9-nonanediamine unit] to [the amount by mole of the 2-methyl-1,8-octanediamine unit] is in the range of 99:1 to 40:60, more preferably in the range of 99:1 to 50:50 and most preferably in the range of 95:5 to 70:30 from the standpoint of the oxidation resistance, the chemical resistance, the heat resistance, the hydrolysis resistance and the property for melt spinning.

When the polyamide forming the polyamide fiber comprises the

1,9-nonanediamine unit and does not comprise the 2-methyl-1,8-octanediamine unit, it is preferable that the amount of the 1,9-nonanediamine unit is in the range of 60 to 100% by mole based on the amount of the entire diamine units constituting the polyamide from the standpoint of the oxidation resistance, the chemical resistance, the heat resistance, the hydrolysis resistance and the property for melt spinning.

The polyamide forming the polyamide fiber may further comprise, where necessary, diamine units other than the 1,9-nonanediamine unit and the 2-methyl-1,8-octanediamine units as long as the objects of the present invention are not adversely affected. Examples of the other diamine unit which may be comprised in the polyamide include diamine units derived from aliphatic diamines such as ethylenediamine, propylenediamine, 1,4-butanediamine, 1,6-hexanediamine, 1,8-octanediamine, 1,10-decanediamine, 1,12-dodecanediamine, 2-methyl-1,5-pentanediamine, 3-methyl-1,5-pentanediamine, 2,2,4-trimethyl-1,6-hexanediamine, 2,4,4-trimethyl-1,6-hexanediamine, 2-methyl-1,8-octanediamine and 5-methyl-1,9-nonanediamine. The polyamide forming the polyamide fiber may comprise the diamine unit described above singly or in combination or two or more.

It is preferable that the polyamide forming the polyamide fiber has an intrinsic viscosity $[\eta]$ in the range of 0.6 to 2.0 dl/g, more preferably in the range of 0.6 to 1.9 dl/g and most preferable in the range of 0.8 to 1.6 dl/g as measured in concentrated sulfuric acid at 30°C since the property for melt spinning and the mechanical properties of the obtained polyamide fiber are excellent.

It is preferable that 10% or more, more preferably 35% or more and

most preferably 70% or more of the chain ends in the polyamide forming the polyamide fiber are sealed from the standpoint of the property for melt spinning in the production of the fiber and the oxidation resistance, the chemical resistance, the heat resistance and the hydrolysis resistance of the obtained polyamide fiber.

For obtaining the fraction of sealed chain ends in the polyamide, the numbers of the chain ends of the carboxyl group and the amino group and the chain end sealed with a chain end sealing agent present in the polyamide are measured and the fraction of sealed chain ends can be obtained from the obtained numbers in accordance with mathematical equation (2) described in EXAMPLES. It is preferable that the numbers of the chain end groups are obtained by obtaining the integral values of the characteristic signals assigned to the chain end groups in accordance with the $^1\text{H-NMR}$, followed by obtaining the numbers of the chain end groups from the obtained values by calculation from the standpoint of the accuracy and the easiness.

The chain end sealing agent for the polyamide is not particularly limited as long as the agent is a monofunctional compound reactive with the amino group or the carboxyl group present at the chain ends of the polyamide molecules. From the standpoint of the reactivity and the stability of the sealed chain ends, monocarboxylic acids and monoamines are preferable as the chain end sealing agent. Among these compounds, monocarboxylic acids are preferable from the standpoint of the easiness of handling.

The monocarboxylic acid which can be used as the chain end sealing agent is not particularly limited as long as the agent can react with amino

group. Examples of the monocarboxylic acid include aliphatic monocarboxylic acids such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, lauric acid, tridecylic acid, myristic acid, palmitic acid, stearic acid, pivalic acid and isobutyric acid; alicyclic
5 monocarboxylic acids such as cyclohexanecarboxylic acid; and aromatic monocarboxylic acids such as benzoic acid, toluic acid, α -naphthalenecarboxylic acid, β -naphthalenecarboxylic acid, methyl-naphthalene carboxylic acid and phenylacetic acid. The above carboxylic acids can be used singly or in combination or two or more. Among the
10 above carboxylic acids, acetic acid, propionic acid, caproic acid, caprylic acid, lauric acid, tridecylic acid, myristic acid, palmitic acid, stearic acid and benzoic acid are preferable from the standpoint of the reactivity, the stability of the sealed chain ends and the price.

To seal the chain ends of the polyamide with the monocarboxylic
15 acid, the amount by mole of the diamine component is set slightly greater than the amount by mole of the dicarboxylic acid component in the preparation of the polyamide so that both chain ends of the polyamide have amino groups, and the monocarboxylic acid is added to the thus obtained polyamide to seal the amino group at the chain ends.

20 When the chain ends of the polyamide is sealed with a monoamine, the monoamine is not particularly limited as long as the monoamine can react with carboxyl group. Examples of the monoamine include aliphatic monoamines such as methylamine, ethylamine, propylamine, butylamine, hexylamine, octylamine, decylamine, stearylamine, dimethylamine, diethylamine, dipropylamine and dibutylamine; and aromatic mono-
25 amines such as aniline, toluidine, diphenylamine and naphthylamine.

The monoamines described above can be used singly or in combination or two or more. Among the above monoamines, butylamine, hexylamine, octylamine, decylamine, stearylamine, cyclohexylamine and aniline are preferable from the standpoint of the reactivity with carboxyl group, the boiling point, the stability of the sealed chain ends and the price.

To seal the chain ends of the polyamide with the monoamine, the amount by mole of the diamine component is set slightly smaller than the amount by mole of the dicarboxylic acid component in the preparation of the polyamide so that both chain ends of the polyamide have carboxyl groups, and the monoamine is added to the thus obtained polyamide to seal the carboxyl group at the chain ends.

It is preferable that the amount of the chain end sealing agent used in the preparation of the polyamide is adjusted in accordance with the intrinsic viscosity $[\eta]$ (the molecular weight) of the polyamide obtained at the end of the process, the fraction of sealed chain ends, the reactivity and the boiling point of the chain end sealing agent and the conditions of the reaction. In general, it is preferable that the chain end sealing agent is used in an amount in the range of about 0.5 to 10% by mole based on the total of the amount by mole of the dicarboxylic acid and the amount by mole of the diamine.

It is preferable that the size of the single fiber in the polyamide fiber constituting the separator for alkaline batteries of the present invention is in the range of 0.01 to 1.0 dtex and more preferably in the range of 0.1 to 0.8 dtex from the standpoint of the property for handling in the production of the non-woven fiber structural material for the separator for alkaline batteries using a paper machine and the property

for holding the alkaline electrolyte, the property for separation and the internal resistance of the obtained separator for alkaline batteries.

It is preferable that the length of the polyamide fiber constituting the separator for alkaline batteries of the present invention is in the range of about 0.5 to 5 mm and more preferably in the range of 1 to 4 mm from the standpoint of the property for dispersion of the polyamide fiber in water and the property for forming the texture in the production of the non-woven fiber structural material for the separator for alkaline batteries using a paper machine.

The processes for producing the polyamide and the fiber comprising the polyamide used in the present invention are not particularly limited and any processes can be used as long as the polyamide and the polyamide fiber having the composition of the structural units described above can be produced. For example, the polyamide can be produced in accordance with the solution polymerization process or the interfacial polymerization process using an acid chloride and the diamine as the raw materials or in accordance with the melt polymerization process, the solid phase polymerization process or the melt extrusion polymerization process using the dicarboxylic acid and the diamine as the raw materials. The obtained polyamide is melt spun and drawn in accordance with a conventional process, cut into a prescribed length and the polyamide fiber for the separator for alkaline batteries can be obtained.

The polyamide and the fiber comprising the polyamide used in the present invention can be advantageously produced, for example, in accordance with the process described in the following. However, the processes for producing the polyamide and the fiber comprising the

polyamide used the present invention are not limited to the process described as the example.

[Example of preparation of a polyamide and a polyamide fiber]

(1) Preparation of a polyamide

5 A chain end sealing agent and a catalyst are added together to the diamine and the dicarboxylic acid at the beginning of the reaction and a nylon salt is formed. The formed nylon salt is polymerized at a temperature of 280°C or lower and a prepolymer having an intrinsic viscosity $[\eta]$ in the range of 0.15 to 0.25 dl/g (in concentrated sulfuric acid,
10 at 30°C) is prepared. The obtained prepolymer is polymerized in accordance with the solid phase polymerization process or the process using a melt extruder until the intrinsic viscosity has a value in the range of 0.6 to 2.0 dl/g. The polyamide for the polyamide fiber can be produced easily in accordance with the above process.

15 In the above process, when the chain end sealing agent and the catalyst are not added at the beginning of the production of the prepolymer but at a stage after the formation of the nylon salt, problems tend to arise in that the suitable balance between the amount by mole of the carboxyl group and the amount by mole of the amino group is lost
20 during the polymerization and crosslinked structures are formed. Therefore, it is preferable that the chain end sealing agent and the catalyst are added at the beginning.

 By adjusting the intrinsic viscosity $[\eta]$ of the prepolymer in the range of 0.15 to 0.25 dl/g described above, the loss of the suitable balance
25 between the amount by mole of the carboxyl group and the amount by mole of the amino group can be prevented and the decrease in the

polymerization rate is suppressed in the post-polymerization step for increasing the molecular weight. Thus, the polyamide having a narrow molecular weight distribution and exhibiting excellent physical properties and property for melt spinning can be obtained.

5 In the above process, when the post-polymerization step for increasing the molecular weight is conducted in accordance with the solid phase polymerization, it is preferable that the polymerization is conducted under a reduced pressure or under a stream of an inert gas. When the polymerization temperature in the post-polymerization step is adjusted in
10 the range of 200 to 250°C, the polyamide having no color and containing no gel can be produced with excellent productivity while the polymerization rate is kept at a great value.

When the final step of the polymerization is conducted using a melt extruder, almost no decomposition of the polyamide takes place and the
15 polyamide can be obtained without degradation by adjusting the polymerization temperature at 370°C or lower.

Examples of the catalyst described above used for producing the polyamide include phosphoric acid, phosphorous acid, hypophosphorous acid, ammonium salts of these acids, salts of these acids with metals such
20 as potassium, sodium, magnesium, vanadium, calcium, zinc, cobalt, manganese, tin, tungsten, germanium, titanium and antimony, and esters of these acids such as ethyl esters, isopropyl esters, butyl esters, hexyl esters, undecyl esters, octadecyl esters, decyl esters, stearyl esters and phenyl esters. Among these compounds, sodium hypophosphite is
25 preferable from the standpoint of the availability and the property for handling.

In the preparation of the polyamide, where necessary, stabilizers and antioxidants may be added during the polymerization or after the polymerization.

(2) Preparation of the polyamide fiber

5 The polyamide fiber is prepared by melt spinning the polyamide obtained above. It is preferable that the melt spinning is conducted using a melt extruder and more preferably using a melt extruder of the screw type. The polyamide obtained above is melted preferably at a temperature in the range of the melting point to 360°C and extruded from
10 nozzles of a die in a fiber shape with a melt residence time of 30 minutes or shorter. The heat decomposition during the spinning is suppressed and the polyamide fiber having the excellent quality can be obtained when the melt temperature and the melt residence time satisfy the above conditions.

15 The polyamide fiber (the thread) spun in the above is drawn by a winding roller or the like. Where necessary, a zone for heating or keeping the temperature may be disposed directly under the nozzles or a cooling zone using a blowing chamber or the like may be disposed. An oil may be applied to the thread formed by the spinning. It is preferable
20 that the melt spinning is conducted in a manner such that the drawn fiber has a birefringence of 20×10^{-3} or smaller. By adjusting the birefringence at 20×10^{-3} or smaller, the polyamide fiber can be drawn sufficiently in the drawing step and the polyamide fiber having a great strength can be obtained.

25 The polyamide fiber obtained above is drawn. The drawing can be conducted by using a conventional apparatus for drawing such as the

heated oil bath, the apparatus for blowing with heated steam, the roller heater, the plate heater of the contact type and the plate heater of the non-contact type. It is preferable that the temperature of the drawing is 270°C or lower and more preferably in the range of 120 to 250°C, and the
5 draw ratio is 2 or greater and more preferably 3 or greater. When the temperature of drawing is higher than 270°C, degradation of the polyamide and reorganization of the crystals take place and the strength of the fiber tends to decrease. Where necessary, following the drawing, the heat treatment at a fixed length, the heat treatment under tension or
10 the heat treatment under relaxation may be conducted at a temperature in the range of 120 to 270°C.

As another process, the object polyamide fiber may be prepared in the single step by the direct drawing after spinning without using the above process.

15 By adjusting the hole diameter of the nozzle in the melt spinning, the amount of spinning of the polyamide and the draw ratio in the series of steps described above for obtaining the polyamide fiber, the polyamide fiber having a size of the single fiber in the range of 0.01 to 1.0 denier which can be advantageously used for the separator for alkaline batteries
20 can be obtained.

The polyamide fiber obtained as described above is cut into a length in the range of 0.5 to 5 mm and short fibers of the polyamide for forming the separator for alkaline batteries of the present invention can be produced.

25 In the present invention, it is necessary that the so-called "solvent-spun cellulose fiber" which is produced by using a spinning

solution prepared by dissolving cellulose into a non-reactive solvent is used as the other main component fiber constituting the separator for alkaline batteries.

5 The "solvent-spun cellulose fiber" is different from the so-called regenerated cellulose fiber which is prepared by chemically converting (modifying) cellulose into a cellulose derivative, followed by regenerating cellulose from the cellulose derivative, such as the conventional viscose rayon and the conventional copper ammonia rayon. The present fiber is a fiber obtained by simply dissolving cellulose into a solvent without
10 chemical conversion (modification), followed by coagulating the obtained solution to obtain cellulose in the fiber shape. From this standpoint, the solvent-spun cellulose fiber used in the present invention is greatly different from fiber and pulp modified with an alkali (mercerized) which are obtained by the treatment with a concentrated alkali, such as
15 mercerized cellulose fiber and mercerized pulp.

Physical properties of the solvent-spun cellulose fiber used in the present invention are greatly different from those of the conventional regenerated cellulose fibers obtained by regeneration from cellulose II (hydrated cellulose) via viscose, such as viscose rayon, polynodic rayon,
20 high tenacity rayon and copper ammonia rayon, and fibrils at the inside of the fiber are well developed into the innermost portion of the fiber.

The solvent-spun cellulose fiber used in the present invention is not particularly limited as long as the fiber is the cellulose fiber prepared in accordance with the solvent-spinning process, in which a spinning
25 solution is prepared by dissolving cellulose into a "non-reactive solvent", i.e., a solvent which dissolves cellulose without causing reactions with

cellulose (without causing chemical modification of cellulose) and the cellulose fiber is obtained by using the prepared spinning solution.

As the cellulose material for obtaining the solvent-spun cellulose fiber, cellulose I (natural cellulose without any modification) alone,
5 cellulose II (hydrated cellulose) alone and mixtures of cellulose I and cellulose II can be used. From the standpoint of the recycling of resources, the cellulose fiber obtained by coagulating the solution of the cellulose material into the fiber shape using cellulose I alone as the cellulose material is preferable.

10 As the non-reactive solvent used for the preparation of the solvent-spun cellulose fiber, any solvent can be used as long as the solvent can dissolve cellulose without causing reactions with cellulose. Examples of the non-reactive solvent include inorganic solvents such as an aqueous solution of zinc chloride, organic solvents such as N-methylmorpholin-
15 oxide as a typical example and mixed solvents of the organic solvent and water. Among these solvents, amine oxides such as N-methylmorpholin-oxide is preferable as the non-reactive solvent from the standpoint of the cost and the environment.

Examples of the solvent-spun cellulose fiber preferably used in the
20 present invention include solvent-spun cellulose fibers which are prepared in a manner such that a spinning solution is prepared by dissolving cellulose in an amine oxide, the prepared spinning solution is subjected to the dry-wet spinning in water, and the obtained fiber is further drawn. Typical examples of the solvent-spun cellulose fiber described above
25 include "TENCEL" (a registered trade name) manufactured by ACORDIS Company in England and "SOLUTION" (a registered trade name)

manufactured by RENZING Company in Austria.

The dry-wet spinning is the process in which the spinning solution is extruded from a die into a gas, which is typically the air, and the extruded fluid is immediately introduced into a coagulating fluid for
5 coagulation. In general, the die is disposed in the gas at a position above the surface of the coagulating fluid by 5 to 200 mm. After the spinning solution extruded from the die is passed through the gas, the spinning solution is introduced into a coagulating bath comprising water or the like and is coagulated.

10 In the present invention, the reason why the oxidation is suppressed remarkably even when the separator is exposed to high temperatures for a long time, for example, even when the separator is stored at high temperatures, and a great positive electrode capacity (the capacity of the battery) can be maintained for a long time when the
15 separator for alkaline batteries is formed using the specific polyamide fiber described above in combination with the solvent-spun cellulose as the main component fibers is not fully elucidated but can be considered as follows.

The solvent-spun cellulose fiber has a great Young's modulus under
20 the wet condition, and flatting in water is small. The degree of crystallization and the orientation are great, and the resistance to alkali is excellent. Therefore, when the solvent-spun cellulose fiber is treated by wet beating in water by using a beater or a refiner, a thin and long material having fibrils is formed, and the formed material having fibrils
25 has a great degree of crystallization and orientation. When the separator for alkaline batteries is produced by using the solvent-spun cellulose fiber

(in particular, the product obtained after the beating treatment) in combination with the polyamide fiber described above, pores are formed. Therefore, it is considered that the separator for alkaline batteries which exhibits the improved property for separation, the excellent resistance to alkalis and the suppressed degradation by oxidation and maintains the great positive electrode capacity (the capacity of the battery) for a long time can be obtained.

In the present invention, cellulose fibers having Canadian standard freeness (CSF) in the range of 100 to 700 ml are preferable from the standpoint of the prevention of the internal short circuit.

From the standpoint of the workability in the production of the separator for alkaline batteries and the property for absorbing the alkaline electrolyte, the property for separation and the property for working by a paper machine of the separator for alkaline batteries, it is preferable that the diameter of the cellulose fiber is in the range of 5 to 20 μm and more preferably in the range of 6 to 15 μm and the length of the cellulose fiber is in the range of 0.5 to 5 mm and more preferably in the range of 1.5 to 4 mm.

In the separator (the non-woven fiber structural material) for alkaline batteries of the present invention, it is necessary that the ratio of the amount by mass of the polyamide fiber to the amount by mass of the cellulose fiber which are described above be in the range of 20:80 to 80:20, preferably in the range of 20:80 to 70:30 and more preferably in the range of 25:75 to 50:50. When the amount of the polyamide fiber is less than 20% by mass, i.e., when the amount of the cellulose fiber exceeds 80% by mass, based on the total of the amounts of the polyamide fiber and the

mass, based on the total of the amounts of the polyamide fiber and the cellulose fiber, the oxidation resistance of the separator for alkaline batteries decreases, and it becomes difficult that the decrease in the capacity of the battery and the decrease in the discharging property in exposure to high temperatures are suppressed. When the amount of the polyamide fiber exceeds 80% by mass, i.e., when the amount of the cellulose fiber is less than 20% by mass, the ability of the separator for alkaline batteries absorbing the alkaline electrolyte decreases and the pore size increases. Therefore, obtaining a great amount of the electric current becomes difficult and the property for preventing the internal short circuit decreases.

In the separator for alkaline batteries of the present invention, it is preferable that the main component fibers comprising the polyamide fiber and the cellulose fiber are adhered together with a binder from the standpoint of the easiness of producing the separator for alkaline batteries and the strength and the property for holding the shape of the obtained separator for alkaline batteries.

As the binder, any of fiber-shaped binders, powder-shaped binders shape and liquid binders can be used. The fiber-shaped binder are preferable since the main component fibers are excellently adhered to each other and the pores in the separator for alkaline batteries can be made finer.

Any fiber-shaped binders can be used as long as the entire portion or a portion of the binder is melted, softened or dissolved at the temperature of heating during the production of the non-woven fiber structural material constituting the separator for alkaline batteries and

the adhesion between the main component fibers and the adhesion between the main component fibers and the fiber-shaped binder can be achieved. Examples of the fiber-shaped binder include polyvinyl alcohol-based fibers, ethylene-vinyl alcohol-based copolymer fibers, 5 polyethylene fibers, polyamide fibers and vinyl chloride-vinyl acetate-based copolymer fibers. The fiber-shaped binder may be used singly or in combination of two or more. Among the above fiber-shaped binders, the polyvinyl alcohol-based fibers and the ethylene-vinyl alcohol-based copolymer fibers are preferable due to the great affinity 10 with the alkaline electrolyte.

As the polyvinyl alcohol-based binder preferable as the fiber-shaped binder, polyvinyl alcohol-based binders having a temperature of dissolution in water in the range of 50 to 90°C and more preferably in the range of 60 to 80°C are preferable. As the ethylene-vinyl alcohol 15 copolymer-based binder, ethylene-vinyl alcohol copolymer-based binders having a melting point in the range of 50 to 130°C and more preferably in the range of 60 to 110°C are preferable.

It is preferable that the size of the fiber-shaped binder is in the range of 0.01 to 1.5 dtex and more preferably in the range of 0.04 to 1.2 20 dtex. When the size of the fiber-shaped binder exceeds 1.5 dtex, the surface area of the fiber decreases and the efficiency of adhesion decreases. Moreover, fine pores in the separator for alkaline batteries are shielded and the internal resistance of the battery increases.

It is preferable that the amount of the fiber-shaped binder is in the 25 range of 3 to 30% by mass and more preferably in the range of 5 to 20% by mass based on the total of the amount by mass of the main component

fibers comprising the polyamide fiber and the cellulose fiber and the amount by mass of the fiber-shaped binder from the standpoint of the efficiency of adhesion and the physical properties and the internal resistance of the obtained separator for alkaline batteries.

5 The separator for alkaline batteries of the present invention may further comprise, where desired, other fibers such as synthetic fibers having a temperature of dissolution in water higher than that of the fiber-shaped binder, examples of which include polyvinyl alcohol-based fibers, polyacrylonitrile fibers, polyolefin fibers, polyvinylidene chloride
10 fibers and polyurethane fibers, rayons such as viscose rayon and chemical fibers such as rayon, cupro and acetate in combination with the above polyamide fiber, the cellulose fiber and the fiber-shaped binder as long as the objects of the present invention are not adversely affected.

 When the separator for alkaline batteries of the present invention
15 is treated with a surfactant, the rate of absorption of the alkaline electrolyte during the assembly of the battery can be increased.

 The process, the apparatus and the conditions for producing the separator for alkaline batteries of the present invention are not particularly limited. Any of the conventional processes which can
20 produce the non-woven fiber structural material from the main fiber components described above and, preferably, using the fiber-shaped binder described above in combination with the main fiber components, can be used. In particular, the wet process using a paper machine is preferable. For example, the separator for alkaline batteries or the
25 non-woven fiber structural material (the material sheet) for the separator for alkaline batteries having the desired shape, dimension, thickness and

the unit weight can be obtained as follows: an aqueous slurry is prepared from the polyamide fiber, the cellulose fiber and the fiber-shaped binder described above; a sheet is prepared from the aqueous slurry using a circular net paper machine or a mold which allows passage of liquids; the liquid is removed from the resultant sheet; and the obtained sheet is dried. It is preferable that the sheet prepared from the aqueous slurry is dried at a temperature in the range of 100 to 140°C.

The shape of the separator for alkaline batteries of the present invention is not particularly limited and various shapes may be used in accordance with the shape in the application. For example, any of shapes of flat paper and non-woven fabrics, a shape of a cylinder, a shape of a cylinder having a bottom and other prescribed shapes can be used.

The unit weight of the separator for alkaline batteries of the present invention can be adjusted in accordance with the type of the battery to which the separator is attached. In general, from the standpoint of the light weight, the property for holding the alkaline electrolyte, the property for separation and the internal resistance, it is preferable that the unit weight is in the range of 20 to 60 g/m² and more preferably in the range of 23 to 45 g/m².

The separator for alkaline batteries of the present invention exhibits excellent property for absorbing the electrolyte (property for holding the electrolyte) since the specific polyamide fiber having the excellent oxidation resistance described above is used as one of the main fiber components in combination with the cellulose fiber. Moreover, the separator is not degraded by oxidation in storage at high temperatures even when the separator is used for alkali batteries using the positive

electrode mix containing compounds having a great oxidizing ability such as nickel oxyhydroxide, and the decrease in the capacity of the battery can be suppressed even when the separator is exposed to high temperatures for a long time, for example, even when the separator is stored at high
5 temperatures.

Therefore, taking advantage of the above properties, the separator for alkaline batteries of the present invention can be particularly effectively used for alkaline manganese batteries using manganese dioxide added with compounds exhibiting great oxidizing ability such as
10 nickel oxyhydroxide as the positive electrode mix. The separator can also be used effectively for batteries other than the alkaline manganese battery such as the silver oxide battery and the electric double layer capacitor batteries.

15 EXAMPLES

The present invention will be described more specifically with reference to examples in the following. However, the present invention is not limited to the examples.

The intrinsic viscosity $[\eta]$ and the fraction of sealed chain ends of
20 polyamides obtained in Preparation Examples 1 to 9 described in the following were measured in accordance with the following methods.

<<Intrinsic viscosity of a polyamide $[\eta]$ >>

A polyamide was dissolved into concentrated sulfuric acid, and sample solutions having concentrations of 0.05, 0.1, 0.2 and 0.4 dl/g were
25 prepared. Inherent viscosities η_{inh} were obtained at 30°C in accordance with the following mathematical equation (1), and the value obtained by

extrapolating the resultant values to the concentration of 0 was used as $[\eta]$.

$$\eta_{inh} = [\ln(t_1/t_0)]/C \quad (1)$$

[In the above equation, t_0 represents the flow time (second) of the solvent,
5 t_1 represents the flow time (second) of the sample solution and C
represents the concentration of the sample solution.]

<<Fraction of sealed chain ends>>

The numbers of carboxyl group and amino group at the chain ends
and the number of the chain end sealed with the chain end sealing agent
10 were measured, and the fraction of sealed chain ends could be obtained in
accordance with the following mathematical equation (2). From the
standpoint of the accuracy and convenience, it was preferable that the
number of each chain end group was obtained from the characteristic
signal assigned to respective chain end groups in accordance with
15 $^1\text{H-NMR}$.

$$\text{Fraction of sealed chain ends (\%)} = [(X-Y)/X] \times 100 \quad (2)$$

[In the above equation, X represents the number of the entire end groups
in the molecular chains, which is, in general, equal to twice the number of
the polyamide molecules, and Y represents the total of the number of
20 carboxyl group left remaining at the chain ends without being sealed and
the number of amino group left remaining at the chain ends without being
sealed.]

To evaluate the properties of separators for alkaline batteries,
alkaline dry cells of size AA were prepared in accordance with the
25 procedures described in Example of Cell Preparation 1 described in the
following using the separators for alkaline batteries obtained in the

following Examples and Comparative Examples. The discharging property of the obtained alkaline dry cells was evaluated in accordance with the method described in the following, and the properties of the separator for alkaline batteries were evaluated based on the obtained result.

« Example of Cell Preparation 1 » [Preparation of an alkaline dry cell]

(1) Nickel oxyhydroxide (the particle diameter: 5 to 15 μm) in an amount of 50 parts by mass, 50 parts by mass of manganese dioxide (the particle diameter: 20 to 50 μm), 5 parts by mass of graphite powder (the particle diameter: 10 to 25 μm), polyethylene powder (the particle diameter: 5 to 15 μm) and 1 part by mass of an aqueous solution of potassium hydroxide (an electrolyte) having a concentration of 40% by mass were mixed by a mixer. After the particle diameter of the resultant mixture was adjusted at the prescribed value, the obtained particulate mixture was molded into a short cylindrical shape, and a positive electrode mix was prepared.

(2) Into a positive electrode can which was used also as the positive terminal, the positive electrode mix having a short cylindrical shape which was prepared in (1) described above was placed under a pressure. Then, a separator having a shape of a cylinder having a bottom which was formed from a sheet prepared by a paper machine in each Example or Comparative Example was inserted at the inside of the positive electrode mix having a short cylindrical shape. The inside of the separator having a shape of a cylinder having a bottom was filled with a negative electrode mix in the gel form which was prepared by mixing 1 part by mass of sodium acrylate, 33 parts by mass of an aqueous solution of potassium hydroxide having a concentration of 40% by mass and 66 parts by mass of

zinc powder. A negative electrode collector was disposed at the central portion of the separator having a shape of a cylinder having a bottom. The open end of the positive electrode can was sealed with a sealing pair made of a resin, to which a negative electrode terminal (a bottom plate) connected to the head portion of the negative electrode collector described above was welded, and a washer made of a metal. Thus, an alkaline dry cell of size AA was prepared.

«Evaluation of the discharging property of an alkaline dry cell»

For the evaluation of the discharging property of an alkaline dry cell, alkaline dry cells of size AA prepared in accordance with the procedures described in Example of Cell Preparation 1 were used immediately after the preparation, after being kept at 25°C for 1 week after the preparation and after being kept at 80°C for 3 days after the preparation. The dry cells were each treated by the continuous discharge at a temperature of the environment of 20°C under an electric current of 1,500 mA, and the time passed until the voltage reached 0.9 V was measured. The discharging property was evaluated as a relative value based on the discharging time of the alkaline dry cell prepared by using the separator of Comparative Example 1 and evaluated immediately after the preparation, which was set at 100.

«Preparation Example 1» [Preparation of a polyamide and polyamide fiber (a₁)]

(1) Into an autoclave having an inner volume of 20 dm³, 2,825 g (17.2 moles) of terephthalic acid, 1,521 g (9.2 moles) of isophthalic acid, 2,391 g (15.1 moles) of 1,9-nonanediamine, 1,956 g (12.4 moles) of

2-methyl-1,8-octanediamine, 268.5 g (2.20 moles) of benzoic acid (the chain end sealing agent), 9.0 g (0.1% by mass based on the amount of the materials forming the polyamide) of sodium hypophosphite hydrate and 2.2 dm³ of distilled water were placed, and the autoclave was purged with
5 nitrogen.

(2) Then, the content of the autoclave was stirred at 100°C for 30 minutes, and the temperature inside the autoclave was raised to 210°C over 2 hours (the pressure inside the autoclave at this temperature was 22 kg/cm²). After the reaction was allowed to proceed in this condition for 1
10 hour, the temperature was raised to 230°C. The reaction was allowed to proceed for 2 hours while the pressure was kept at 22 kg/cm² by slowly releasing generated steam and the temperature was kept at 230°C.

(3) The pressure was lowered to 10 kg/cm² over 30 minutes. The reaction was allowed to proceed under this pressure for 1 hour, and a
15 prepolymer was prepared. The obtained prepolymer was dried under a reduced pressure at 100°C for 12 hours, and the dried prepolymer was pulverized into particles having a size of 2 mm or smaller.

(4) The pulverized prepolymer obtained in (3) described above was subjected to the solid phase polymerization under a reduced pressure of
20 132.9 Pa (0.1 mmHg) at 230°C for 10 hours, and a polyamide was prepared. The intrinsic viscosity $[\eta]$ and the fraction of sealed chain ends of the prepared polyamide were measured in accordance with the methods described above and were found to be 0.65 and 88%, respectively.

(5) The polyamide obtained in (4) described above was supplied to a melt
25 spinning apparatus of the screw extrusion type. Fibers were spun through a spinning die (having 100 holes each having a round nozzle

having a diameter of 0.1 mm) at a temperature of spinning by extrusion of 300°C and wound. The thread obtained from the fibers was drawn to a length 3.2 times the original length and heated by passing through a drawing bath (the first bath; the temperature: 85°C) and a heating bath
5 (the second bath; the temperature: 95°C), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.1 dtex was obtained.

(6) The tow obtained in (5) described above was cut into fibers having a length of 2 mm, and polyamide fiber (a_1) having a short fiber shape was
10 prepared.

«Preparation Example 2» [Preparation of a polyamide and polyamide fiber (a_2)]

(1) Into an autoclave having an inner volume of 20 dm³, 2,989 g (18.0
15 moles) of terephthalic acid, 1,609 g (9.7 moles) of isophthalic acid, 2,402 g (15.2 moles) of 1,9-nonanediamine, 1,975 g (12.5 moles) of 2-methyl-1,8-octanediamine, 67.6 g (0.55 moles) of benzoic acid (the chain end sealing agent), 9.0 g (0.1% by mass based on the amount of the materials forming the polyamide) of sodium hypophosphite hydrate and
20 2.2 dm³ of distilled water were placed, and the autoclave was purged with nitrogen.

(2) Then, the content of the autoclave was stirred at 100°C for 30 minutes, and the temperature inside the autoclave was raised to 210°C over 2 hours (the pressure inside the autoclave at this temperature was 22
25 kg/cm²). After the reaction was allowed to proceed in this condition for 1 hour, the temperature was raised to 230°C. The reaction was allowed to

proceed for 2 hours while the pressure was kept at 22 kg/cm² by slowly releasing generated steam and the temperature was kept at 230°C.

(3) The pressure was lowered to 10 kg/cm² over 30 minutes. The reaction was allowed to proceed under this pressure for 1 hour, and a prepolymer was prepared. The obtained prepolymer was dried under a reduced pressure at 100°C for 12 hours, and the dried prepolymer was pulverized into particles having a size of 2 mm or smaller.

(4) The pulverized prepolymer obtained in (3) described above was subjected to the solid phase polymerization under a reduced pressure of 132.9 Pa (0.1 mmHg) at 230°C for 10 hours, and a polyamide was prepared. The intrinsic viscosity $[\eta]$ and the fraction of sealed chain ends of the prepared polyamide were measured in accordance with the methods described above and were found to be 1.40 and 65%, respectively.

(5) The polyamide obtained in (4) described above was melt spun, drawn and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.8 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of winding were adjusted so that the polyamide fiber in which the single fiber had the prescribed size could be obtained.

(6) The tow obtained in (5) described above was cut into fibers having a length of 3 mm, and polyamide fiber (a₂) having a short fiber shape was prepared.

«Preparation Example 3» [Preparation of a polyamide and polyamide fiber (a₃)]

- (1) Into an autoclave having an inner volume of 20 dm³, 4,497 g (27.1 moles) of terephthalic acid, 3,495 g (22.1 moles) of 1,9-nonanediamine, 874 g (5.5 moles) of 2-methyl-1,8-octanediamine, 134.8 g (1.11 moles) of benzoic acid (the chain end sealing agent), 9.0 g (0.1% by mass based on the amount of the materials forming the polyamide) of sodium hypophosphite hydrate and 2.2 dm³ of distilled water were placed, and the autoclave was purged with nitrogen.
- (2) Then, the content of the autoclave was stirred at 100°C for 30 minutes, and the temperature inside the autoclave was raised to 210°C over 2 hours (the pressure inside the autoclave at this temperature was 22 kg/cm²). After the reaction was allowed to proceed in this condition for 1 hour, the temperature was raised to 230°C. The reaction was allowed to proceed for 2 hours while the pressure was kept at 22 kg/cm² by slowly releasing generated steam and the temperature was kept at 230°C.
- (3) The pressure was lowered to 10 kg/cm² over 30 minutes. The reaction was allowed to proceed under this pressure for 1 hour, and a prepolymer was prepared. The obtained prepolymer was dried under a reduced pressure at 100°C for 12 hours, and the dried prepolymer was pulverized into particles having a size of 2 mm or smaller.
- (4) The pulverized prepolymer obtained in (3) described above was subjected to the solid phase polymerization under a reduced pressure of 132.9 Pa (0.1 mmHg) at 230°C for 10 hours, and a polyamide was prepared. The intrinsic viscosity $[\eta]$ and the fraction of sealed chain ends of the prepared polyamide were measured in accordance with the methods described above and were found to be 1.00 and 74%, respectively.
- (5) The polyamide obtained in (4) described above was melt spun, drawn

and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.3 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of winding were adjusted so that the polyamide fiber in which the single fiber had the prescribed size could be obtained.

(6) The tow obtained in (5) described above was cut into fibers having a length of 2 mm, and polyamide fiber (a_3) having a short fiber shape was prepared.

«Preparation Example 4» [Preparation of a polyamide and polyamide fiber (a_4)]

(1) In accordance with the same procedures as those conducted in Preparation Example 3, a polyamide having an intrinsic viscosity $[\eta]$ of 1.00 and a fraction of sealed chain ends of 76% was prepared.

(2) The polyamide obtained in (1) described above was melt spun, drawn and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 1.0 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of winding were adjusted so that the polyamide fiber in which the single fiber had the prescribed size could be obtained.

(3) The tow obtained in (2) described above was cut into fibers having a length of 5 mm, and polyamide fiber (a_4) having a short fiber shape was prepared.

«Preparation Example 5» [Preparation of a polyamide and polyamide fiber (a_5)]

(1) In accordance with the same procedures as those conducted in Preparation Example 3, a polyamide having an intrinsic viscosity $[\eta]$ of 1.00 and a fraction of sealed chain ends of 75% was prepared.

(2) The polyamide obtained in (1) described above was melt spun, drawn and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.5 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of winding were adjusted so that the polyamide fiber in which the single fiber had the prescribed size could be obtained.

(3) The tow obtained in (2) described above was cut into fibers having a length of 2 mm, and polyamide fiber (a_5) having a short fiber shape was prepared.

«Preparation Example 6» [Preparation of a polyamide and polyamide fiber (a_6)]

(1) In accordance with the same procedures as those conducted in Preparation Example 3, a polyamide having an intrinsic viscosity $[\eta]$ of 1.00 and a fraction of sealed chain ends of 74% was prepared.

(2) The polyamide obtained in (1) described above was melt spun, drawn and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.8 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of

winding were adjusted so that the polyamide fiber in which the single fiber had the prescribed size could be obtained.

(3) The tow obtained in (2) described above was cut into fibers having a length of 3 mm, and polyamide fiber (a_6) having a short fiber shape was prepared.

«Preparation Example 7» [Preparation of a polyamide and polyamide fiber (a_7)]

(1) Into an autoclave having an inner volume of 20 dm³, 1,798 g (10.8 moles) of terephthalic acid, 2,698 g (16.3 moles) of isophthalic acid, 3,495 g (22.1 moles) of 1,9-nonanediamine, 874 g (5.5 moles) of 2-methyl-1,8-octanediamine, 134.8 g (1.11 moles) of benzoic acid (the chain end sealing agent), 9.0 g (0.1% by mass based on the amount of the materials forming the polyamide) of sodium hypophosphite hydrate and 2.2 dm³ of distilled water were placed, and the autoclave was purged with nitrogen.

(2) A polyamide was prepared in accordance with the same procedures as those conducted in Preparation Example 1 (2) to (4). The intrinsic viscosity $[\eta]$ and the fraction of sealed chain ends were measured in accordance with the methods described above and were found to be 1.00 and 77%, respectively.

(3) The polyamide obtained in (2) described above was melt spun, drawn and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.8 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of winding were adjusted so that the polyamide fiber in which the single

fiber had the prescribed size could be obtained.

(4) The tow obtained in (3) described above was cut into fibers having a length of 3 mm, and polyamide fiber (a₇) having a short fiber shape was prepared.

5

«Preparation Example 8» [Preparation of a polyamide and polyamide fiber (a₈)]

(1) Into an autoclave having an inner volume of 20 dm³, 4,497 g (27.1 moles) of terephthalic acid, 874 g (5.5 moles) of 1,9-nonanediamine, 3,495 g (22.1 moles) of 2-methyl-1,8-octanediamine, 134.8 g (1.11 moles) of benzoic acid (the chain end sealing agent), 9.0 g (0.1% by mass based on the amount of the materials forming the polyamide) of sodium hypophosphite hydrate and 2.2 dm³ of distilled water were placed, and the autoclave was purged with nitrogen.

15 (2) A polyamide was prepared in accordance with the same procedures as those conducted in Preparation Example 1 (2) to (4). The intrinsic viscosity $[\eta]$ and the fraction of sealed chain ends were measured in accordance with the methods described above and were found to be 1.00 and 75%, respectively.

20 (3) The polyamide obtained in (2) described above was melt spun, drawn and heated in accordance with the same procedures as those conducted in Preparation Example 1 (5), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.8 dtex was obtained. In the preparation of the polyamide fiber, the speed of spinning and the speed of winding were adjusted so that the polyamide fiber in which the single
25 fiber had the prescribed size could be obtained.

(4) The tow obtained in (3) described above was cut into fibers having a length of 3 mm, and polyamide fiber (a₉) having a short fiber shape was prepared.

5 «Preparation Example 9» [Preparation of a polyamide and polyamide fiber (a₉)]

(1) Into an autoclave having an inner volume of 20 dm³, 4,876 g (33.4 moles) of adipic acid, 3,954 g (34.1 moles) of hexamethylenediamine, 166.4 g (1.36 moles) of benzoic acid (the chain end sealing agent), 9.0 g (0.1% by mass based on the amount of the materials forming the polyamide) of sodium hypophosphite hydrate and 2.2 dm³ of distilled water were placed, and the autoclave was purged with nitrogen.

(2) A polyamide was prepared in accordance with the same procedures as those conducted in Preparation Example 1 (2) to (4). The intrinsic viscosity [η] and the fraction of sealed chain ends were measured in accordance with the methods described above and were found to be 1.00 and 80%, respectively.

(3) The polyamide obtained in (2) described above was supplied to a melt spinning apparatus of the screw extrusion type. Fibers were spun through a spinning die (having 100 holes each having a round nozzle having a diameter of 0.1 mm) at a temperature of spinning by extrusion of 300°C and wound. The thread obtained from the fibers was drawn to a length 3.2 times the original length and heated by passing through a drawing bath (the first bath; the temperature: 85°C) and a heating bath (the second bath; the temperature: 95°C), and a tow composed of a polyamide fiber in which the single fiber had a size of 0.8 dtex was

obtained.

(4) The tow obtained in (3) described above was cut into fibers having a length of 3 mm, and polyamide fiber (a₉) having a short fiber shape was prepared.

5 The conditions and the results of Preparation Examples 1 to 9 are shown together in Tables 1 and 2 in the following.

Table 1

10	Preparation Example	1	2	3	4	5
	[Material for polyamide]					
	Acid component (% by mole)					
	terephthalic acid	65	65	100	100	100
15	isophthalic acid	35	35	-	-	-
	adipic acid	-	-	-	-	-
	Diamine component (% by mole)					
	1,9-nonanediamine	55	55	80	80	80
	2-methyl-1,8-octanediamine	45	45	20	20	20
20	hexamethylenediamine	-	-	-	-	-
	Ratio of amounts by mole of acid component to diamine component	96:100	99:100	98:100	98:100	98:100
	Chain end sealing agent (benzoic acid) (% by mole) ¹⁾	8.0	2.0	4.0	4.0	4.0
25	[Physical property of polyamide]					
	intrinsic viscosity [η]	0.65	1.40	1.00	1.00	1.00
	fraction of sealed chain ends (%)	88	65	74	76	75
30	[Polyamide fiber]					
	type	a ₁	a ₂	a ₃	a ₄	a ₅
	size of single fiber (dtex)	0.1	0.8	0.3	1.0	0.5
	length of fiber (mm)	2	3	2	5	2

1): % by mole based on the total of the amount by mole of the dicarboxylic acid unit and the amount by mole of the diamine unit.

Table 2

5	Preparation Example	6	7	8	9
	[Material for polyamide]				
	Acid component (% by mole)				
10	terephthalic acid	100	40	100	-
	isophthalic acid	-	60	-	-
	adipic acid	-	-	-	100
	Diamine component (% by mole)				
	1,9-nonanediamine	80	80	20	-
15	2-methyl-1,8-octanediamine	20	20	80	-
	hexamethylenediamine	-	-	-	100
	Ratio of amounts by mole of acid component to diamine component	98:100	98:100	98:100	98:100
20	Chain end sealing agent (benzoic acid) (% by mole) ¹⁾	4.0	4.0	4.0	4.0
	[Physical property of polyamide]				
	intrinsic viscosity [η]	1.00	1.00	1.00	1.00
25	fraction of sealed chain ends (%)	74	77	75	80
	[Polyamide fiber]				
	type	a ₆	a ₇	a ₈	a ₉
	size of single fiber (dtex)	0.8	0.8	0.8	0.8
30	length of fiber (mm)	3	3	3	3

1): % by mole based on the total of the amount by mole of the dicarboxylic acid unit and the amount by mole of the diamine unit.

The cellulose fibers and the fiber-shaped binders used in Examples and Comparative Examples are described in the following and abbreviated as shown also in the following:

Cellulose fiber

5 (1) Cellulose fiber b_1 :

“TENCEL” (a registered trade name) manufactured by ACORDIS Company; (CSF=400 ml)

(2) Cellulose fiber b_2 :

10 “TENCEL” (a registered trade name) manufactured by ACORDIS Company; (CSF=300 ml)

(3) Cellulose fiber b_3 :

Mercerized wood pulp; (CSF=400 ml)

(4) Cellulose fiber b_4 :

15 Cotton linter (manufactured by TAIHEI SEISHI Co., Ltd.; CSF=400 ml)

Fiber-shaped binder

(1) Fiber-shaped binder c_1 :

20 A polyvinyl alcohol fiber (VINYLON) (manufactured by KURARAY Co., Ltd.; “VPB 105-1×3”) (the size of the single fiber = 1.0 dtex; the length of the fiber: 3 mm; the temperature of dissolution in water: 70°C)

(2) Fiber-shaped binder c_2 :

25 A polyvinyl alcohol fiber (VINYLON) (manufactured by KURARAY Co., Ltd.) (the size of the single fiber = 0.08 dtex; the length of the fiber: 2 mm; the temperature of dissolution in water: 70°C)

(3) Fiber-shaped binder c_3 :

An ethylene-vinyl alcohol copolymer fiber (manufactured by KURARAY Co., Ltd.) (the size of the single fiber = 0.05 dtex; the length of the fiber: 2 mm; the softening point: 95°C)

5 «Example 1»

(1) To 99,000 parts by mass of water at a temperature of 18°C, 20 parts by mass of polyamide fiber a_1 obtained in Preparation Example 1, 70 parts by mass of cellulose fiber b_1 and 10 parts by mass of fiber-shaped binder c_1 were added and uniformly mixed under stirring, and a material
10 for paper making in the slurry form having a content of solid substances of 0.1% by mass was prepared. A sheet was prepared by a paper machine of the Tappi type and dried by a cylinder drier at 110°C, and a separator paper for batteries having a unit weight of 31 g/m² was prepared.

(2) Using the separator paper for batteries obtained in (1) described
15 above, a separator having a cup shape (a cylindrical shape having a bottom) of the size matching the size of the alkaline dry cell of size AA was prepared. An alkaline dry cell of size AA was prepared using the prepared separator, and the discharging property of the prepared alkaline dry cell was evaluated. The result is shown in Table 3 in the following.

20

«Examples 2 to 5»

(1) Materials for paper making in the slurry form having a concentration of solid substances of 0.1% by mass were prepared using polyamides a_2 to a_5 obtained in Preparation Examples 2 to 5, respectively, each in a
25 relative amount shown in Table 3 in place of polyamide fiber a_1 and the cellulose fiber and the fiber-shaped binder shown in Table 3 in relative

amounts also shown in Table 3, and separator papers for batteries shown in Table 3 were prepared in accordance with the same procedures as those conducted in Example 1 (1).

(2) Using the separator papers for batteries obtained in (1) described above, separators having a cup shape of the size matching the size of the alkaline dry cell of size AA were prepared. Alkaline dry cells of size AA were prepared using the prepared separators, and the discharging property of the prepared alkaline dry cells was evaluated. The results are shown in Table 3 in the following.

« Comparative Example 1 »

(1) A material for paper making in the slurry form having a concentration of solid substances of 0.1% by mass was prepared using polyamide a₆ obtained in Preparation Example 6 in a relative amount shown in Table 3 in place of polyamide fiber a₁ and the cellulose fiber and the fiber-shaped binder shown in Table 4 in relative amounts also shown in Table 4, and a separator paper for batteries shown in Table 4 was prepared in accordance with the same procedures as those conducted in Example 1 (1).

(2) Using the separator paper for batteries obtained in (1) described above, a separator having a cup shape of the size matching the size of the alkaline dry cell of size AA was prepared. An alkaline dry cell of size AA was prepared using the prepared separator, and the discharging property of the prepared alkaline dry cell was evaluated. The result is shown in Table 4 in the following.

« Comparative Example 2 »

(1) To 99,000 parts by mass of water at a temperature of 18°C, 25 parts by mass of a polyvinyl alcohol fiber (VINYLON) (manufactured by KURARAY Co., Ltd.; "VPB 083×3"; the size of the single fiber = 0.8 dtex; the length of the fiber: 3 mm; the temperature of dissolution in water: 100°C or higher) and 60 parts by mass of cellulose fiber b₄ as the main fiber components and 15 parts by mass of fiber-shaped binder c₁ were added and uniformly mixed under stirring, and a material for paper making in the slurry form having a content of solid substances of 0.1% by mass was prepared. A sheet was prepared by a paper machine of the Tappi type and dried by a cylinder drier at 110°C, and a separator paper for batteries having a unit weight of 31 g/m² was prepared.

(2) Using the separator paper for batteries obtained in (1) described above, a separator having a cup shape of the size matching the size of the alkaline dry cell of size AA was prepared. An alkaline dry cell of size AA was prepared using the prepared separator, and the discharging property of the prepared alkaline dry cell was evaluated. The result is shown in Table 4 in the following.

« Comparative Examples 3 to 5 »

(1) Materials for paper making in the slurry form having a concentration of solid substances of 0.1% by mass were prepared using polyamides a₇ to a₉ obtained in Preparation Examples 7 to 9, respectively, each in a relative amount shown in Table 4 in place of polyamide fiber a₁ and the cellulose fiber and the fiber-shaped binder shown in Table 4 in relative amounts also shown in Table 4, and separator papers for batteries shown

in Table 4 were prepared in accordance with the same procedures as those conducted in Example 1 (1).

- (2) Using the separator papers for batteries obtained in (1) described above, separators having a cup shape of the size matching the size of the alkaline dry cell of size AA were prepared. Alkaline dry cells of size AA were prepared using the prepared separators, and the discharging property of the prepared alkaline dry cells was evaluated. The results are shown in Table 4 in the following.

Table 3

	Example	1	2	3	4	5
5	[Composition of separator]					
	Main component fiber					
	polyamide fiber					
	type	a1	a2	a3	a4	a5
	amount (% by mass)	20	30	40	65	50
10	cellulose fiber					
	type	b1	b1	b1	b2	b1
	amount (% by mole)	70	60	50	28	35
	polyvinyl alcohol fiber					
	type	-	-	-	-	-
15	amount (% by mass)	-	-	-	-	-
	Fiber-shaped binder					
	type	c1	c1	c1	c2	c3
	amount (% by mass)	10	10	10	7	15
20	[Discharging property of alkaline battery]					
	immediately after being prepared	98	98	99	103	100
	after being kept at 25°C for 1 week	97	97	97	101	98
25	after being kept at 80°C for 3 days	92	92	93	95	94

Table 4

Comparative Example	1	2	3	4	5
5 [Composition of separator]					
Main component fiber					
polyamide fiber					
type	a6	-	a9	a7	a8
amount (% by mass)	30	-	30	30	30
10 cellulose fiber					
type	b3	b4	b3	b3	b3
amount (% by mole)	60	60	60	60	60
polyvinyl alcohol fiber					
type	-	vinylon 1)	-	-	-
15 amount (% by mass)	-	25	-	-	-
Fiber-shaped binder					
type	c1	c1	c1	c1	c1
amount (% by mass)	10	15	10	10	10
20 [Discharging property of alkaline battery]					
immediately after being prepared	99	100	98	97	99
after being kept at 25°C for 1 week	97	98	99	96	96
25 after being kept at 80°C for 3 days	72	56	64	69	68

1): Polyvinyl alcohol fiber (manufactured by KURARAY Co., Ltd.; "VINYLON")
 (the size of the single fiber: 0.8 dtex; the length of the single fiber: 3 mm;
 the temperature of dissolution in water: 70°C)

As shown in Tables 3 and 4, the alkaline batteries of Examples 1 to 5 exhibited remarkably improved discharging properties after being kept at the high temperature of 80°C since the separators used in the alkaline batteries were formed with the polyamide fibers and the solvent-spun cellulose fiber (TENCEL) as the main component fibers, wherein the polyamide fibers were formed with the polyamides composed of terephthalic acid unit in an amount of 60% by mole or more of the dicarboxylic acid unit and 1,9-nonanediamine unit in an amount of 40% by mole or more of the diamine unit, and in particular, the polyamides composed of terephthalic acid unit in an amount of 60% by mole or more of the dicarboxylic acid unit, 1,9-nonanediamine unit in an amount of 40% by mole or more of the diamine unit and the 2-methyl-1,8-octanediamine unit in combination with the 1,9-nonanediamine unit, and these main component fibers were used in relative amounts in the range of 20:80 to 80:20 (the ratio by mass). It is shown by the above results that the separators for alkaline batteries of the present invention prepared in Examples 1 to 5 exhibited remarkably excellent properties for separation in storage at high temperatures.

In contrast, the alkaline battery in Comparative Example 1 exhibited the discharging property after being kept at a high temperature of 80°C inferior to that of the alkaline batteries of Examples 1 to 5 since the cellulose fiber was not the solvent-spun cellulose fiber but the mercerized wood pulp although the separator for alkaline batteries was formed with the polyamide fiber and the cellulose fiber, wherein the polyamide fiber was formed with the polyamide composed of terephthalic acid unit in an amount of 60% by mole or more of the dicarboxylic acid

unit, 1,9-nonanediamine unit in an amount of 40% by mole or more of the diamine unit and the 2-methyl-1,8-octanediamine unit in combination with the 1,9-nonanediamine unit.

5 The alkaline battery in Comparative Example 2 exhibited the discharging property after being kept at a high temperature of 80°C markedly inferior to that of the alkaline batteries of Examples 1 to 5 since the separator was formed with the polyvinyl alcohol fiber and the cellulose fiber as the main component fibers.

10 The alkaline battery of Comparative Example 3 exhibited the discharging property after being kept at a high temperature of 80°C markedly inferior to that of the alkaline batteries of Examples 1 to 5 since the polyamide forming the polyamide fiber in the separator for alkaline batteries was composed of the adipic acid unit, i.e., an aliphatic dicarboxylic acid unit, and the hexamethylenediamine unit, and the
15 cellulose fiber was a cellulose fiber other than the solvent-spun cellulose fiber.

The alkaline battery of Comparative Example 4 exhibited the discharging property after being kept at a high temperature of 80°C inferior to that of the alkaline batteries of Examples 1 to 5 since, in the
20 polyamide forming the polyamide fiber in the separator for alkaline batteries, the relative amount of the terephthalic acid unit was 40% by mole which was less than 60% by mole, and the cellulose fiber was a cellulose fiber other than the solvent-spun cellulose fiber.

The alkaline battery of Comparative Example 5 exhibited the
25 discharging property after being kept at a high temperature of 80°C inferior to that of the alkaline batteries of Examples 1 to 5 since, in the

polyamide forming the polyamide fiber in the separator for alkaline batteries, the relative amount of the 1,9-nonanediamine unit was 20% by mole which was less than 40% by mole, and the cellulose fiber was a cellulose fiber other than the solvent-spun cellulose fiber.

5

INDUSTRIAL APPLICABILITY

Since the separator for alkaline batteries of the present invention is formed by using the specific polyamide fiber described above and the specific cellulose fiber (the solvent-spun cellulose fiber) as the main component fibers, the separator for alkaline batteries of the present invention exhibits not only the excellent property for absorbing the alkaline electrolyte (the excellent property for holding liquids) but also the suppressed degradation by oxidation even when the separator is used for an alkaline battery using, as the positive electrode mix, manganese dioxide added with an agent having a great oxidizing ability for enhancing the discharging property under a great load such as nickel oxyhydroxide and excellently maintains the function as the separator even when the separator is exposed to high temperatures for a long time, for example, even when the separator is stored at high temperatures. Therefore, the alkaline battery using the separator for alkaline batteries of the present invention can maintain the great capacity of the positive electrode (the capacity of the battery) for a long time and can be used for various types of portable information instruments requiring the excellent discharging property under a great load such as digital cameras.

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